

KINETICS AND ISOTHERM STUDIES FOR EVALUATING ADSORPTION CAPACITY OF CERAMIC POTTERY WASTE FOR THE REMOVAL OF Cu(II) IN AQUEOUS SYSTEM

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ABSTRACT

Heavy metal pollution has become one of the most serious environmental problems today. Increased industrial activities have resulted in the generation of large amounts of wastewater polluted with heavy metals. In the present research work, adsorptive capacity of ceramic pottery waste (CPW) for the removal of Cu(II) ions in aqueous medium has been studied. Batch method has been employed to investigate the effects of various adsorption controlling parameters such as contact time (5-90 min), pH (2-10) of solution, metal ions concentration (10-200 mg/L) and adsorbent dose (0.1-1.0 g) on adsorption of Cu(II) ions onto CPW. The optimum set of conditions for maximum adsorption of Cu(II) ions were found to be initial concentration 50mg/L, dosage 0.5 g and pH 6.0. The maximum adsorption of Cu(II) ions by CPW was found to be 93.8 %. The adsorption data was fitted best to the Freundlich model ($R^2 = 0.990$). Langmuir monolayer adsorption capacity of ceramic pottery waste for Cu(II) was found to be 2.747 mg/g. The experimental data was best described pseudo- second order model. EDX analysis indicated the presence of copper ions on adsorbent surface. These results suggested that ceramic pottery waste could be employed as efficient adsorbent for the removal of Cu(II) from aqueous solution and contaminated water sources.

Key words: Ceramic pottery waste, adsorption, monolayer, Langmuir, Freundlich, pseudo second orders etc.

I INTRODUCTION

Water is essential for life on our planet. Increasingly, human activities threaten the water sources on which we all depend. One of the most threatening health hazards is the pollution through heavy metal [1]. Heavy metals have been extensively released into the environment due to rapid industrialization and have created a major global concern. Unlike organic contaminants, heavy metals are non-biodegradable; they accumulate in living organisms causing adverse effects to many vital functions. They can move through the biological chains there by reaching human beings and leading to chronic and acute ailments.

Copper, as an essential trace element, is required by biological systems for the activation of some enzymes during photosynthesis [2]. In animal cells it is mainly concentrated in the mitochondria, DNA, RNA, and the nucleus [3]. Mining, metallurgy and industrial applications are the major sources of copper exposure in the environment [4]. Copper is highly toxic because it is non-biodegradable and carcinogenic and a neurotoxic disorder commonly known as “Wilson’s disease” caused due to deposition of copper in the lenticular nucleus of the brain. Addition to it absorption of copper compounds by inhalation causes congestion of the nasal mucosa, gastritis, diarrhoea and toxic symptoms such as chronic lung damage. Continuous exposure of copper may lead to kidney damage and even death [5]; [6]. Copper is also toxic to a variety of aquatic organisms even at very low concentrations.

In recent years, various methods such as chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation flocculation and electrochemical methods, for the removal of copper from aqueous solutions have been extensively studied. But adsorption is recognized as an effective, simple and economic method for removal of heavy metals from aqueous solutions [7]. In this regards, multiple researchers studied the effectiveness of various type of clay based and other adsorbents in removing heavy metals ions including copper from aqueous solutions such as kaolinite [8], montmorillonitic and calcareous clays [9], bentonite [10]; [11], illite [12], montmorillonite [13], natural clay [14], Pottery glaze [15], tea mugs [16], Roasted china clay (RCC) [17], saw dust [18], rice husk [19]. The utilization of one waste material to control pollution caused by another is of high significance in the remediation of environmental problems. The use of waste material as adsorbent is particularly beneficial for the development of cost-effective process for heavy metal removal from wastewaters which should reduce the prices of products and benefit the environment. Therefore, in present study ceramic pottery waste has been employed as adsorbent for the removal of Cu(II) ions from aqueous solutions.

II METHODOLOGY

2.1 Collection and preparation of adsorbent

In Khurja (U.P), ceramic pottery industries manufactured pots, toys and other decorative articles from ceramic powder which is a mixture of china clay, animal bone, quartz and feldspar. First ceramic powder is converted into a semi-solid paste to mould it into various shapes for making articles. Then moulded articles are subjected to intense heating called firing to provide rigidity. After firing the paste becomes hard and porous. But during the process of firing, some of the articles breaks or get deshaped which are thrown away as waste. This thrown away waste were collected, grinded into fine particles and sieved through 100 mesh size and used as adsorbent to depart Cu(II) ions from aqueous solutions.

2.2 Characterisation of adsorbent

The surface morphology of the ceramic pottery waste before and after adsorption of Cu(II) was studied by scanning electron microscopy (SEM). The SEM micrographs were recorded using Scanning Tunnelling Microscope, JEOL-JSM 6510 LV at University Sophisticated Instrumentation Facility (USIF), AMU, Aligarh. The determination of

elemental composition of CPW before and after adsorption of Cu(II) ions was carried out using, The Oxford Instruments INCA X-sight energy dispersive X-ray (EDX) spectrometer equipped with SEM.

The FTIR studies were conducted on CPW by Perkin-Elmer Fourier Transformer Spectrophotometer (FTIR) Version 10.03.08 using KBr pellet technique in the wavelength range $450\text{--}4000\text{ cm}^{-1}$, at Instrumentation Lab, Department of Chemistry, Aligarh Muslim University (AMU), Aligarh.

2.3 Determination of point of zero charge (pH_{pzc})

The point of zero charge (pH_{pzc}) of the CPW was determined by solid addition method with DDW and 0.1 N KNO_3 solutions [20]. The 50 ml DDW was transferred into a series of conical flasks and the initial pH (pH_i) of these solutions were roughly adjusted between 2 to 10 by adding either 0.1 N HCl or 0.1 N NaOH solutions. The initial pH (pH_i) of these solutions was then measured accurately by using pH meter. After that 0.5 gm of adsorbent was added into each flask and allowed to equilibrate for 24 hours with intermittent manual shaking. After attaining equilibrium solution was filtered and the final pH (pH_f) of the supernatant liquid was then noted. The difference between initial and final values ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f$) were plotted against pH_i , the point of intersection of resulting curve with abscissa at which ΔpH is zero, gave the point of zero charge (pH_{pzc}). The same procedure was repeated using 0.1 N KNO_3 solutions.

2.4 Adsorbate solution

A stock solution of 500 mgL^{-1} of Cu(II) was prepared by dissolving required amount of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in double distilled water in a 500 ml standard flask. This stock solution was used to prepare the working solutions of desired concentrations for all experiments. The pH values of the solutions was adjusted by adding 0.1N NaOH or 0.1N HCl.

2.5 Adsorption studies

Batch process were conducted at room temperature $27 \pm 1^\circ\text{C}$ to study the adsorption of Cu(II) ions by ceramic pottery waste. An accurately weighed 0.5g of CPW was placed in 100 ml stopper conical flask containing 50 ml of Cu(II) ions solution of concentration 50 mg/L. These solutions were shaken in a rotary shaker for required time to attain equilibrium. All the experiments such as effect of pH, adsorbent dose, contact time were conducted at room temperature with 50 ml Cu(II) ions solutions of 50 mg/L except during the study of effect of concentration where 10 to 200 mg/L Cu(II) ions concentration solutions were used. The final concentration of metal ions in the solution was analysed by Atomic Absorption Spectrophotometer (AAS). The amount of metal ion adsorbed was calculated by subtracting final concentration from initial concentration.

The removal percentage (R%) of Cu(II) ions and adsorption capacity, $q_e(\text{mg/g})$ of CPW were calculated for each run by the following expression

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100$$

$$q_e = \frac{(C_i - C_e)}{m} \times V$$

where, C_i is the initial concentration of metal ions in the solution (mg/L), C_e is the equilibrium concentration of metal ions (mg/L), V is the volume of the solution (L) taken, m is the mass of the adsorbent (g) used.

III RESULTS AND DISCUSSION

3.1 Characterisation of adsorbent

3.1.1 SEM-EDX analysis

Scanning electron microscope analysis was carried out to examine the porosity and surface morphology of untreated and Cu(II) treated CPW. The SEM images of the untreated and Cu(II) treated CPW are shown in fig. 1 and 2. It can be clearly observed that surface of CPW is irregular and porous and thus revealing the amorphous nature of adsorbent. The morphology of surface is slightly changed after adsorption. Before adsorption, surface appeared to be less dense with light grey patches but after adsorption surface became slightly regular and denser with dark grey patches showing the adherence of Cu(II) ions on the surface by means of physisorption [21]; [22]. EDX spectra were obtained to analyse the elemental composition of CPW before and after adsorption of Cu(II) and shown in fig 3 & 4. Spectrum before adsorption clearly indicated the peaks for the presence of oxygen, calcium, and silicon as major constituents. EDX spectra after adsorption showed a peak of Cu(II) confirming adsorption of Cu(II) on to the surface of ceramic pottery waste. The weight percentage of different constituents obtained from EDX analysis before and after Cu(II) adsorption is reported in table 1.

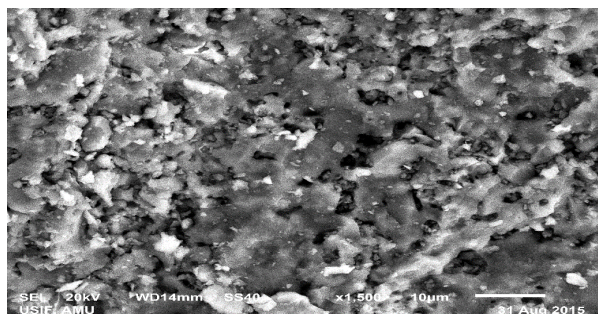


Fig.1 SEM images of CPW before adsorption of Cu(II)

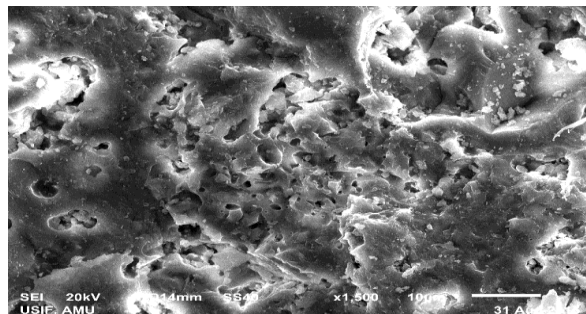


Fig.2 SEM images of CPW after adsorption of Cu(II)

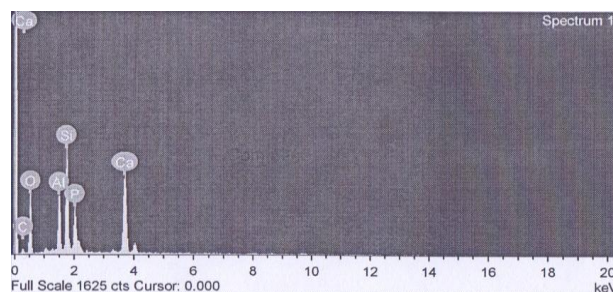


Fig. 3 EDX spectra of CPW before adsorption of Cu(II)

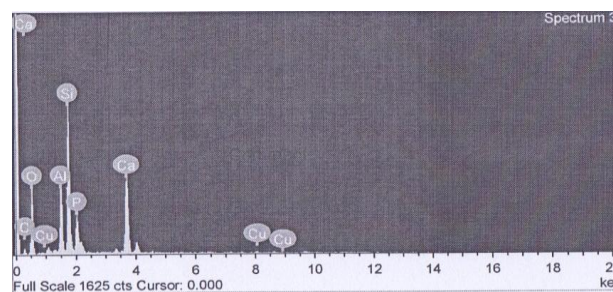


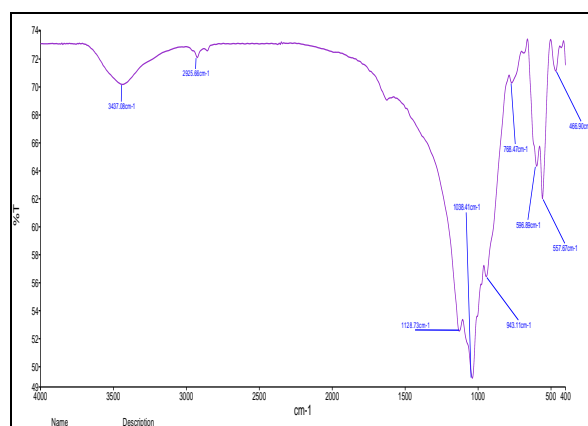
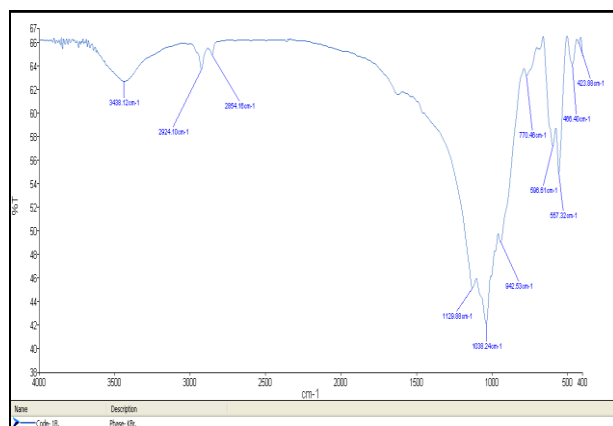
Fig. 4 EDX spectra of CPW after adsorption of Cu(II)

Table 1: EDX analysis of ceramic pottery waste before and after adsorption of Cu(II)

Elements	Before adsorption		After adsorption	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	6.77	11.23	7.91	13.19
O	49.38	61.48	46.35	58.01
Al	6.86	5.07	7.20	5.34
Si	13.35	9.47	17.09	12.18
P	6.91	4.44	5.41	3.50
Ca	16.72	8.31	14.77	7.38
Cu	---	---	1.27	0.40
Total	100.00	100.00	100.00	100.00

3.1.2FTIR Analysis

FTIR is an important technique to determine the type of any functional (binding) group present on the surface of the adsorbent. The FTIR spectra of ceramic pottery waste before and after adsorption of Cu(II) are shown in fig. 5 & 6. The spectra shows a broad band around 3441.91 cm^{-1} which is attributed to the surface -OH group of silanol groups (-Si-OH) and adsorbed water molecules on the surface. A small peak around at 2925.09 cm^{-1} indicates the presence of stretched C-H bond. Peak at 1506.72 cm^{-1} show the presence of C=C bending. Comparison of untreated and Cu(II) treated FTIR spectra of Adsorbent showed the disappearance of some peaks at 3441.91 cm^{-1} , 2925.09 cm^{-1} , 1506 cm^{-1} which indicates that functional groups were involved in adsorption process. All the changes in the spectra of treated ceramic pottery waste are due to the metal bonding process on the surface of adsorbent.


Fig. 5 FTIR graph of CPW before adsorption of Cu(II) Fig. 6 FTIR graph of CPW after adsorption of Cu(II)

3.2 Batch studies

3.2.1 Effect of contact time and metal ions concentration

The influence of initial Cu(II) ions concentration on adsorption is shown in fig. 7. It was found that adsorption capacity of ceramic pottery waste as usual increased with an increase in initial Cu(II) ions concentration. It may be

due to the fact that increase in concentration gradient between the bulk solution and adsorbent surface lower the resistance to mass transfer of Cu(II) ions from liquid to solid phase. The maximum adsorption capacity of ceramic pottery waste at equilibrium were found to be 1.0, 2.41, 4.69, 6.91, 9.19, 11.05, 12.99, 14.79 and 16.28 mg/g at initial Cu(II) ions concentration of 10, 25, 50, 75, 100, 150, 175 and 200 mg/L, respectively. It is also evident from the fig. 7 that adsorption percentage of Cu(II) ions decreased from 100 to 81.4 % with the increase of initial concentration of copper from 10 mg/L to 200 mg/L. It may be due to the saturation of active sites of adsorbent at certain metal ions concentration. The effect of interaction time of Cu(II) ions with the surface of ceramic pottery waste on adsorption of Cu(II) ions is shown in fig 8. The contact time reached to equilibrium was found to be dependent on initial concentration of Cu(II) up to 50 mg/L and then became independent at higher concentration. This may be due to the fact that vacant sites of adsorbent adsorbed Cu(II) ions rapidly at lower concentration but at higher concentration adsorption of copper occurred by slower process (diffusion) into the inner sites of adsorbent. The equilibrium time for the maximum removal of Cu(II) ions (93.8%) from aqueous solution was found to be 30 minutes at concentration 50 mg/L. But at higher concentration it will require more contact time for the maximum removal of Cu(II) ions.

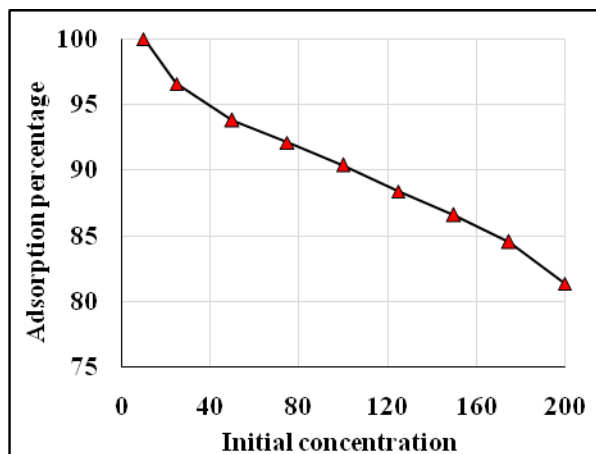


Fig. 7 Effect of Cu(II) ion concentration on adsorption

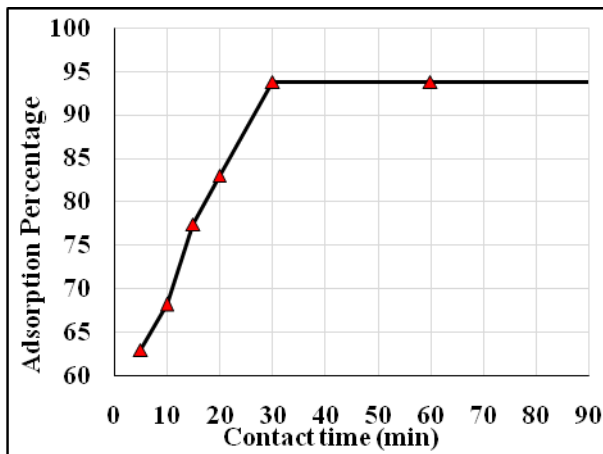
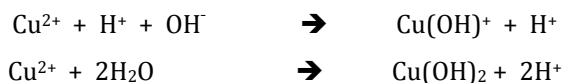


Fig. 8 Effect of contact time on adsorption of Cu(II)

3.2.2 Effect of pH of the solution

Effect of solution pH containing Cu(II) ions on adsorption of Cu(II) by ceramic pottery waste is shown in fig 9. It has been observed that Cu(II) ions uptake by ceramic pottery waste is strongly affected by pH of the solution. The amount of Cu(II) adsorbed was found to increase from 11.4% to 93.8% on increasing pH from 1 to 6 and then decrease slowly on further increase in pH. The variation in the adsorption of Cu(II) with respect to pH can be explained by considering the initial pH (pH_i), final pH or equilibrium pH (pH_f), and speciation of metal ions in the solution [23]. At pH 1, Cu^{2+} ions compete with H^+ ions for binding sites of adsorbent, therefore the adsorption of Cu(II) ions was less (11.4%) at low pH. When the initial pH of the solution raises, the adsorption percentage increased quickly and reached maximum of 93.8%, at pH 6 which is possibly due to little less competition of Cu^{2+}

ions and H^+ ions. Further increase in pH of the solution up to pH 8 results slightly decrease in the adsorption of Cu(II) ions (91.52%). A similar trend was continuing when pH increases to 10. The decrease in the adsorption of Cu(II) at $pH > 6$ can be explained on the basis of Cu(II) speciation at different pH values. The chemical species of Cu(II) formed at different pH values are Cu^{2+} at $pH=2-4$, $Cu(OH)^+$ at $pH=4-6$, $Cu(OH)_2$ at $pH=6-10$ and $Cu(OH)_3^-$ at $pH=10-12$ [24]; [25]. The speciation suggested that majority of the copper is adsorbed in pH range 4-6 in the form of Cu^{2+} ions and copper hydroxide species due to micro precipitation as shown below



Moreover, the pH of point of zero charge, pH_{zpc} has an important influence on adsorption processes. The surface of adsorbent was positive when $pH < pH_{zpc}$, neutral when $pH = pH_{zpc}$ and negative at $pH > pH_{zpc}$ [26]. The data plotted in fig. 10 indicated that the pH_{zpc} value of ceramic pottery waste was 5.4, showing that the surface was negatively charged above this pH and hence fairly large amount of Cu(II) ions (93.8% at pH 6) were adsorbed

3.2.3 Effect of adsorbent dose

The effect of dose of ceramic pottery waste on adsorption capacity and percentage adsorption of Cu(II) is shown in fig 11. Percent adsorption increased while adsorption capacity, q_e (mg/g) decreased when adsorbent dose increased from 0.1 to 1.0 g. The adsorption percentage increases upto 99.20 % at 1 g of adsorbent dose. This might be due to the increase in the number of sites available for adsorption [27]. The adsorption capacity decreases from 16.05 mg/g to 2.48 mg/g on increasing adsorbent dose from 0.1 g to 1.0 g. The decrease in adsorption capacity with an increasing adsorbent dose might be due to the fact that at lower adsorbent dose almost all the adsorption sites are saturated by the Cu(II) ions but at higher adsorbent dose, the adsorption sites would be excessive for the adsorption reaction since the concentration Cu(II) ions as well as the volume of the solution are constant. Thus, amount of Cu(II) adsorbed per unit mass of adsorbent was decreased [28].

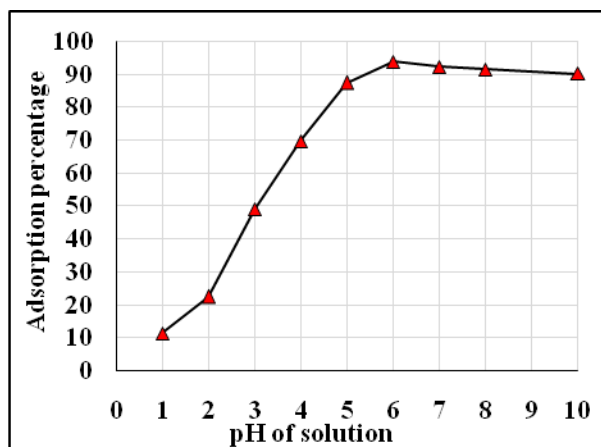


Fig. 9 Effect of solution pH on adsorption of Cu(II)

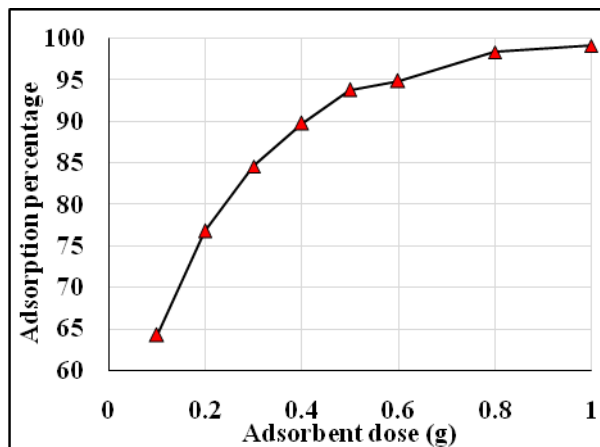


Fig. 11 Effect of dose on adsorption of Cu(II)

3.3 Adsorption isotherms

The Adsorption isotherm curve is an invaluable curve describing the phenomena governing the retention (or release) or mobility of the adsorbent from the aqueous phase to a solid phase at constant temperature and pH [29]; [30]. Adsorption of Cu(II) ions on ceramic pottery waste was carried out at concentration ranging from 10 to 200 mgL⁻¹ at pH 6 for 30 minutes of equilibrium time and obtained data was analysed with Langmuir [31], Freundlich [32] and Temkin [33]; [34] adsorption isotherms which are shown in fig. 12, 13 and 14. The values of R² and other parameters of adsorption isotherms (Table 2) indicated that adsorption of Cu(II) onto ceramic pottery waste was best fitted to Freundlich isotherm model (R²=0.990) and higher value of K_f (K_f= 2.722) indicated higher adsorption capacity of ceramic pottery waste for adsorption of Cu(II) ions. Moreover the higher value of correlation coefficient for Langmuir (R² = 0.945), and Temkin (R² = 0.955) isotherm model also indicated that adsorption of Cu(II) ions on ceramic pottery waste occurs on heterogeneous surface of ceramic pottery waste by formation of monolayer followed by multilayer formation with uniform heat of adsorption [34-36].

The essential characteristic of the Langmuir isotherm is expressed in terms of a dimensionless constant or equilibrium parameter, R_L.

$$R_L = 1/(1 + b C_i)$$

where, b is the Langmuir constant and C_i is the initial concentration of metal ions in the solution.

According to McKay et al. 1982 [37], R_L values indicate the nature of adsorption of metal ions on the surface of adsorbent. The R_L value between 0 to 1 indicates that adsorption process is favourable, R_L equal to 0 indicate irreversible process and R_L < 0 then the adsorption process is unfavourable. The R_L value for obtained data is 0.0038 indicated that adsorption of Cu(II) on CPW is favourable.

Table: 2 Langmuir, Freundlich, Temkin and D-R isotherm constants for the adsorption of Cu(II)

Metal	Langmuir isotherm				Freundlich isotherm			Temkin isotherm		
	q _m	B	R ²	R _L	n	K _F	R ²	A	B	R ²
Cu ²⁺	2.747	6.622	0.946	0.0038	1.934	2.722	0.990	1.466	3.824	0.955

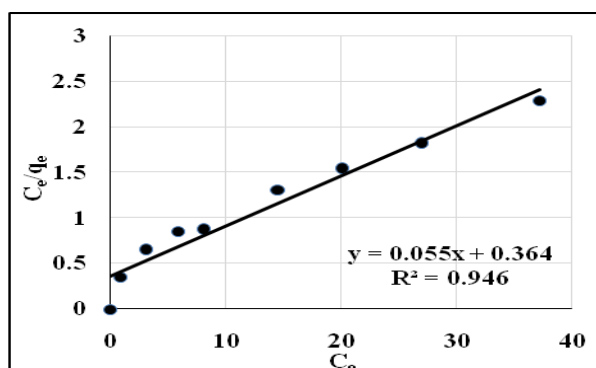


Fig. 12 Langmuir Adsorption Isotherm

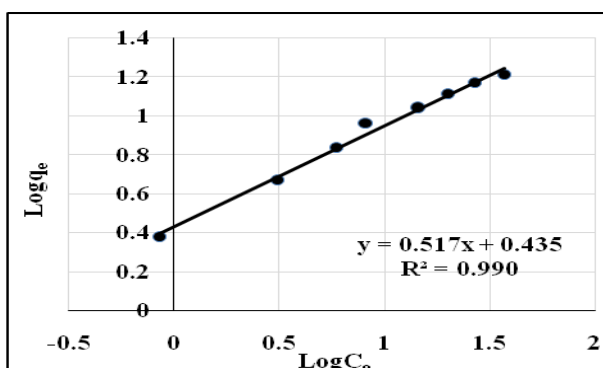


Fig. 13 Freundlich Adsorption Isotherm

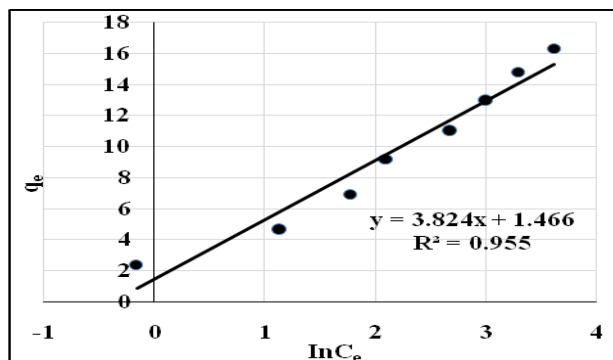


Fig. 14 Temkin Adsorption Isotherm

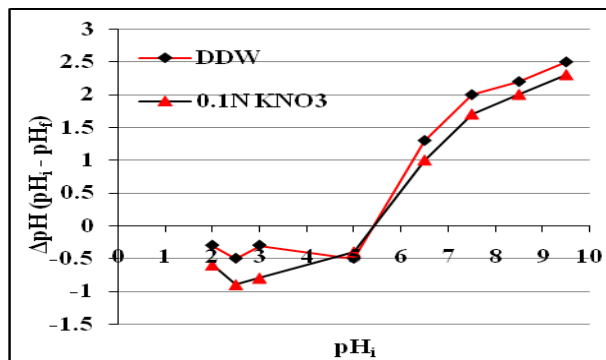


Fig. 10 Point of Zero Charge of CPW

3.4 Adsorption kinetics

The evaluation of kinetic models is an important aspect for designing and optimization of water and wastewater treatment process as it relates the adsorbate uptake rate with bulk concentration [38]; [39]. To investigate the mechanism of adsorption of adsorbate species on the surface of adsorbent and rate controlling steps, the kinetic data was analysed by using the pseudo first-order kinetic model express by Lagergren [40], pseudo second order kinetic model [41] and Intra-particle diffusion model [42].

It had been observed from linearised plots shown in fig. 16, 17 and 18 and values of R^2 for pseudo first order ($R^2 \approx 0.852$), pseudo second order ($R^2 \approx 0.999$) and intra particle diffusion ($R^2 \approx 0.682$) that adsorption of Cu(II) ions by ceramic pottery waste was best described by pseudo second order kinetic model. The values of constants and other parameters mentioned in table 3 indicated that adsorption of Cu(II) ions by ceramic pottery waste is mainly occur by physical adsorption followed by chemisorption of Cu(II) ions as described by pseudo second order model.

Table 3 Pseudo-first order, Pseudo-second order and Inter-particle diffusion model constants

Metal	Pseudo-first order			Pseudo-second order			Intra-particle diffusion		
	q_e	K_1	R^2	q_e	K_2	R^2	I	K_d	R^2
Cu^{2+}	0.3915	84.139	0.852	4.854	0.0703	0.999	3.140	0.175	0.682

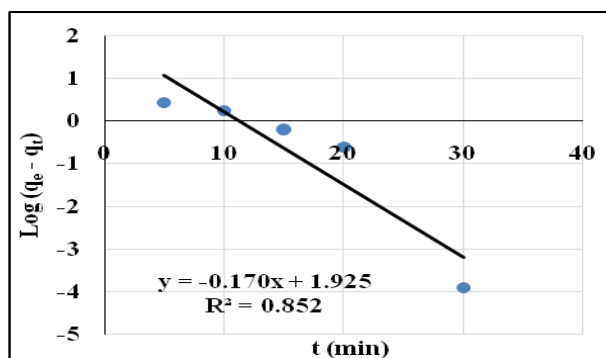


Fig. 16 Pseudo-First Order Model

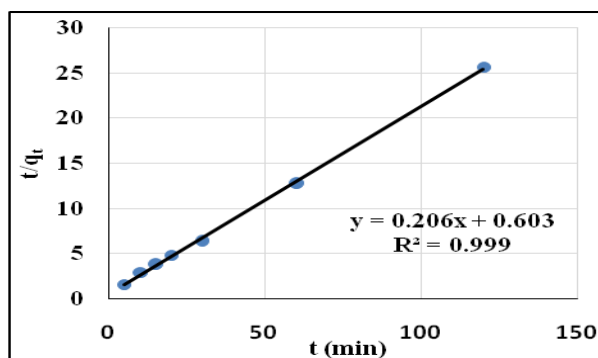


Fig. 17 Pseudo-Second Order Model

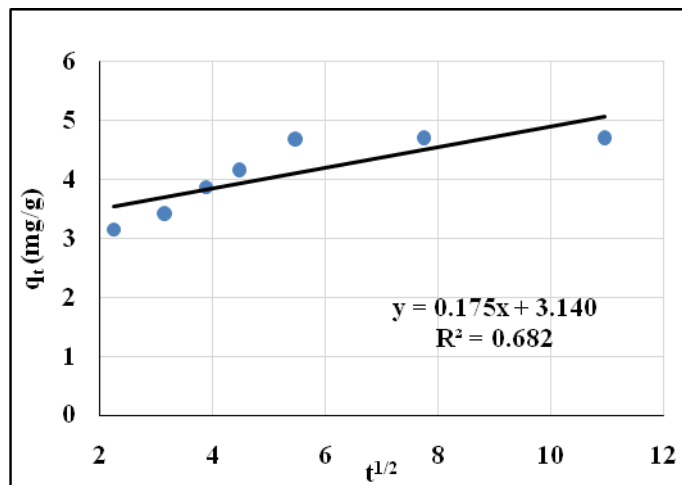


Fig. 18 Intra-Particle Diffusion Model

IV CONCLUSION

Studies found that ceramic pottery waste can be effectively applied for the removal of Cu(II) ions from aqueous solution. The kinetics of metal adsorption by adsorbent was fast, reaching 93.80 % within 30 minutes of contact time. The adsorption of Cu(II) ions was found to be pH dependent and maximum amount of the copper (93.80 %) was removed at pH ranging 4-6. Experimental data of adsorption isotherms showed the better applicability of Langmuir and Freundlich model than Temkin model as indicated by the high values of correlation coefficients (R^2). Higher value of K_f ($K_f = 2.722$) indicated higher adsorption capacity of ceramic pottery waste for adsorption of Cu(II) ion. Kinetic studies showed that adsorption of Cu(II) ions on ceramic pottery waste was best described by pseudo second order kinetic model. Thus, it could be concluded that the ceramic pottery waste is a potential and active adsorbent for the removal of copper ions from aqueous solution and can be employed for industrial waste water remediation.

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